Hindawi
Journal of Chemistry
Volume 2018, Article ID 5942081, 8 pages
https://doi.org/10.1155/2018/5942081

Research Article

Primary Investigation into the Occurrence of Hydroxymethylfurfural (HMF) in a Range of Smoked Products

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Received 15 June 2018; Revised 25 October 2018; Accepted 11 November 2018; Published 5 December 2018

Academic Editor: Annalisa De Girolamo

5-Hydroxymethylfurfural (HMF) is produced in foods through many different pathways. Recently, studies have revealed its potential mutagenic and carcinogenic properties. Determination of HMF was originally used as an indicator of both the extent of thermal processing a food had undergone and food quality. It has been identified in a variety of food products such as bread, breakfast cereals, fruit juices, milk, and honey. In addition to the thermal processes that lead to the formation of HMF during thermal treatment, food smoking also creates conditions that result in the formation of HMF. This can take place within the food due to the elevated temperatures associated with hot smoking or by the proximity of the products of the pyrolysis of the wood matrix that is used for smoking (cold smoking). This may lead to further contamination of the product by HMF over and above that associated with the rest of the preparation process. Until now, there have been no studies examining the relation between the smoking procedure and HMF contamination in smoked food. This study is a primary investigation measuring HMF levels in three categories of smoked food products, cheese, processed meat, and fish, using HPLC-UV. The amount of HMF found in all three product categories supports our hypothesis that HMF levels are due to both internal pathways during processing and external contamination from the smoke generation matrix (wood) employed. The results ranged from 1 ppb (metsovone traditional Greek smoked cheese) to 4 ppm (hot-smoked ready-to-eat mackerel). Subsequently for smoked cheese products, a correlation was found between HMF and phenolic compounds generated by the smoking procedures and identified by SPME-GCMS. It was observed that cheese samples that had higher concentrations of HMF were also found to have higher concentrations of syringol and cresols. It is important therefore to understand the smoking procedure's effect on HMF formation. This will aid in the development of mitigation strategies to reduce HMF formation while retaining the flavour of the smoked products.

1. Introduction

Food smoking is one of the oldest techniques used for the preservation and flavouring of food [1]. Nowadays, such processing is used to improve the organoleptic properties of some food by providing unique flavours [2] originating from the smoke applied, usually by burning wood. Smoking can also alter the colour of foods and promote dehydration, which affects the texture and reduces the bacterial growth. Products that are usually smoked are fish and meat, but these techniques are also applied to cheeses and spices [3].

The burning of wood results in pyrolysis/thermal degradation of its main constituents: cellulose, hemicellulose, and lignin. More than 400 volatile compounds have been found in the smoke of wood, with phenols mainly being responsible for the smoky flavour [4]. A range of factors have been found to influence the smoking process. These include the temperature during the pyrolysis, the wood type (hardwood or softwood), the part of the wood (heartwood or sapwood), the moisture concentration of the wood, and the presence of air during the process [5]. Hot smoking and cold smoking are natural vaporous methods utilising smoke

produced during combustion under different conditions. The temperature for hot smoking processes is usually in the range 55°C to 80°C, and the duration is short. On the contrary, cold smoking takes place over longer periods and can last for days, at temperatures between 15°C to 25°C [2, 4]. The type of polysaccharide present in the wood leads to particular degradation products. Hemicellulose constitutes 20–35% of wood mass, and it mainly contains hexoses and pentoses connected by β-(1,4) bonds. Compounds produced by the pyrolysis of hemicellulose are mainly furans and carboxylic acids, together with aldehydes that give smoked products their characteristic brown colour. Cellulose is a linear polymer of glucose monomeric units connected by β-(1,4) bonds that constitute approximately 40–50% of softwoods and hardwoods. The pyrolysis of cellulose, depending on the burning temperature, can lead to different products such as anhydrous sugars at lower temperatures and furans, pyrans, and glycoaldehyde at higher temperatures [6]. Lignin, a cross-linked polymer of several phenylpropanoids constitutes 20–25% of wood matrix and provides to the smoke phenolic compounds mainly syringol (2,6-dimethoxy-phenol), eugenol (2-methoxy-4-(prop-2-en-1-yl)phenol), isoeugenol (2-methoxy-4-(prop-1-en-1-yl-phenol), guaiacol (2-methoxyphenol), *p*-cresol (4-methylphenol), and phenol. It has been reported that they could be used as indicators of the temperature and duration of the smoking process [7]. Phenols and cresols are produced from further degradation of guaiacols. Syringol levels are higher from the pyrolysis of hardwoods compared to softwoods as the lignin structure is different between the two types of wood with the former containing more syringol [8].

Among other components, 5-hydroxymethylfurfural (HMF) has been identified in wood smoke [9]. There are two main mechanisms of HMF production during the burning of the wood, either the dehydration of hexoses under mild acidic conditions or formed as an intermediate in the Maillard reaction [10].

During pyrolysis, cellulose initially depolymerises forming several anhydrous sugars, mainly levoglucosan. Different levels of levoglucosan result from different burning sources. Subsequently, the thermal degradation of levoglucosan leads to the 1,6- glycosidic bond cleavage and the subsequent formation of glucopyranose by rehydration. There are two pathways to produce HMF. The first pathway includes the rearrangement reaction of 1,6-anhydro-β-D-glucopyranose and the second results from the thermal degradation of levoglucosan. Additionally, further reactions of HMF lead to the production of furfural and formaldehyde by dehydroxymethylation of the furan ring. In addition, according to [11], phenol and benzene are produced from rearrangement reactions of HMF [12].

The other main route to the formation of HMF is the Maillard reaction. The Maillard reaction plays an important role in the taste and appearance of food and occurs during cooking. The Maillard reaction is a complex network of nonenzymatic reactions with different pathways. Maillard starts when an amino group from an amino acid or a protein condenses with a reducing sugar leading to Amadori rearrangement products. At a later stage, 1,2-enolization occurs, and HMF is an intermediate by-product under weak alkaline conditions [13]. Subsequently, HMF reacts further with nitrogen-containing compounds and polymerises giving nitrogenous polymers known as melanoidins, which are responsible for the brown colouration of the food surfaces. The parameters mainly responsible for the quantity and quality of the browning as a consequence of the Maillard reaction are the sugar and amino group source, the extent and type of thermal processing, and pH [14]. Caramelisation, a controlled pyrolysis of sugars, is another nonenzymatic browning reaction that occurs due to thermal treatment and can also lead to HMF formation [15].

HMF has already been identified and measured in many food products such as dried fruits, breads, jams, coffee, caramel, fruit juices, cookies, breakfast cereals, milk, and honey. A number of influences on its formation have been discovered. Examples are, in cookies, the relationship between sugars, mainly glucose, and HMF concentration is linear. For fruit juices, the acidity during hydrolysis was found to be an important factor [16–21]. In honey, measurement of HMF is an indicator of quality age and thermal treatment, and there is a strict regulatory limit. The Honey (Scotland) Regulations 2015, for example, place a limit of not more than 40 mg/kg for all honey except baker's honey and not more than 80 mg/kg for honey from tropical regions. In addition, it has been reported that HMF could be produced when bees are fed with sucrose syrup with an acidic flavour additive [22].

Determination of HMF levels in food products has become important as HMF is metabolised in human body mainly to 5-hydroxymethylfurfuroic acid (HMFA) [23] and to 5-sulfoxymethylfurfural (SMF) [24, 25]. The sulphuric group of the SMF can be removed easily, resulting in the production of an ester with genotoxic and mutagenic effects. This ester further reacts with DNA, RNA, and proteins leading to their damage. Work has been conducted using in vitro and in vivo experiments in animals to identify the extent of the carcinogenic properties of SMF [26–30]. Rats fed with honey with different concentrations of HMF showed adverse health effects as the HMF concentration increased [31].

In this paper, an initial investigation into HMF presence in smoked food products was conducted. We also report our attempt to link the extent and the type of smoking by comparing the phenolic compounds produced during smoking with the different levels of HMF.

2. Materials and Methods

2.1. Materials. The food samples were purchased from local retailers in the Dundee area. Formic acid was purchased from Sigma-Aldrich (St. Louis, MO, USA), 5-(hydroxymethyl)furfural (HMF) was from Fisher Scientific (98%, ACROS Organics™, USA), and the Carrez clarification kit was obtained from Merck (Darmstadt, Germany).

2.2. Sampling. An appropriate sampling technique was used for each of the different sample types. For the cheeses,

an 8 cm^3 cube was cut from the body of the cheese and grated. For processed meats, a portion size slice (8 cm × 8 cm × 2 mm) was used. For fish, the flesh was separated from the skin and each treated was separately. Approximately 25 g of each sample was weighed on an analytical balance (Fisherbrand™ Analytical Balances, UK), freeze-dried (Edwards Freeze Dryer Micro Modulyo, USA), ground (WARING, commercial blender, Aberdeen), and subsequently stored at −20°C until required.

2.3. HMF Analysis. The method used for HMF determination was that of Fiore et al. [32] with some modification. Briefly, 0.5 g of the ground sample was placed in a 50 mL centrifuge tube (Conical, Foam Rack, Sterile, Blue Cap, PP, Fisherbrand, USA). 9 mL of Ultrapure water (UPW) water (with 0.1% formic acid) was added followed by 0.5 ml of Carrez I (potassium ferrocyanide) and 0.5 ml Carrez II (zinc acetate). The mixture was homogenised (IKA Dispersers T 18 digital ULTRA-TURRAX®, USA) for 1 minute and then centrifuged for 10 minutes at 4000 rpm at 4°C (Jouan CR3.12 Refrigerated Benchtop Centrifuge, USA). The supernatant was collected into a 50 mL centrifuge tube. Another 5 mL of UPW was added to the precipitate, and the solution was homogenized and centrifuged as above. This last procedure was repeated one more time after collecting the supernatant. From the combined supernatant layers, 1 mL was transferred to an Eppendorf tube (Fisherbrand, 1.5 mL) and centrifuged for 10 minutes at 14000 rpm 4°C (Eppendorf centrifuge 5417R, Canada). The supernatant was collected and passed through a Minisart 0.2 μm syringe filter (15 mm) into HPLC vials (10 mm Screw, 2 mL, Phenomenex) and analysed by HPLC with the equipment which consisted of a Thermo Scientific (Germany) Ultimate 3000 Pump, Dionex DDA-100 diode array detector, and a Dionex autosampler ASI-100 (San Jose, CA). The mobile phase was methanol: UPW (90 : 10) at a flow rate of 0.8 mL/min under isocratic conditions. The column employed was the Synergy 4 μm Hydro-RP 80 A, 25 × 4.6 cm (Phenomenex, USA). The diode array detector was set to read absorbance at 280 nm and 313 nm. For the calculation of concentration of HMF, a calibration curve was constructed with the HMF range of 20 to 1000 ppb (equation $y = 0.0029x$ and $R^2 = 0.9951$).

2.4. Volatile Compounds Analysis. For the detection of volatile compounds, the method of Guillen and Errecalde [33] was used with modifications. Briefly, 2.00 g of the dry sample was placed in a SPME vial. The instrument used was a QP2010 HS-SPME-GCMS fitted with an AOC-5000 autosampler (Shimadzu, Tokyo, Japan). The SPME fibre employed was a PDMS/DVB from Supelco (UK) and used as follows: 10 min of incubation at 60°C followed by 30 min extraction time and 10 min desorption time. A 30 m, 0.25 mm id, 0.25 μm film thickness Zebron ZB-wax capillary column (Phenomenex, USA) was used with the carrier gas (He) set at a total flow of 94 mL/min and a column flow of 1.78 ml/min. The initial column oven temperature was 40°C rising to 60°C at 4°C·min^{-1} (2 min hold) and then up to 190°C at 2°C·min^{-1} and 230°C at 5°C·min^{-1} (15 min hold) for a total run time of 97 min. The injection temperature was 250°C; the injection mode was splitless and the sampling time 1 minute. The ion source temperature was 200°C, interface temperature 250°, solvent cut time 4.5 min, and mass range 33–495. Finally, the ionization voltage was 70 eV. The analytes were identified by comparing their mass spectra with those recorded in NIST 147.

2.5. Statistical Analysis. For the statistical analysis, XLStat (version 2014.5.03, Addinsoft, NY) was used. Significant differences between the samples with a confidence interval of 95% were performed by using a Tukey test, and for the correlation between HMF concentration and the percentage of volatiles, principal component analysis (PCA) was used.

3. Results and Discussion

3.1. HMF. The analysis of HMF using HPLC with diode array detection at 280 nm and 313 nm was performed on three different groups of smoked products (cheese, processed meat, and fish). There were clear indications of the presence of HMF in all three categories. The range of concentrations varied from 4 ppb (metsovone cheese) up to 3000 ppb (mackerel). The different nature of the samples (cheese, processed meat, and fish) along with other factors such as the type of smoking (hot/cold smoking) or use of smoke condensates and the type of burning matrix (hardwoods, softwoods, and herbs) are considered to be responsible for the different concentration levels of HMF that were identified.

3.1.1. Occurrence of HMF in Cheese Products. In Figure 1, the mean concentrations and standard deviations of HMF in the cheese samples are presented. Samples C1 and C2 had the highest mean concentrations (657 ppb and 475 ppb, respectively), while sample C3 had the lowest mean concentration of 4 ppb. For samples C4, C5, and C6, the mean concentrations ranged from 48 ppb to 88 ppb. C1, C2, and C3 (German, Dutch, and Greek cheeses, respectively) had characteristic brown rinds, the source of which can be attributed to the Maillard reaction or the formation of aldehydes during thermal decomposition [34]. It is interesting to note that sample C3 (metsovone, Greek) had the lowest concentration of HMF. Metsovone is a traditional smoked Greek cheese of protected designation of origin (PDO). It is cold smoked for 1–2 days after maturation with natural smoke from burning grasses, leaves, and herbs of the area. However, samples C1 and C2 (German and Dutch cheeses) are smoked with wood as the burning material. These differences in the smoke generation material may be responsible for the observed concentrations of HMF. Sample C4 (Austrian cheese) was a processed cheese produced by mixing smoked cheddar and smoked butter, but the final product is not smoked; thus, this different process of production might be the cause of the low level of HMF found. Finally, samples C5 and C6 are Scottish cheddars from the same producer (Orkney) single and triple smoked, respectively. The smoke is produced naturally from wood from the

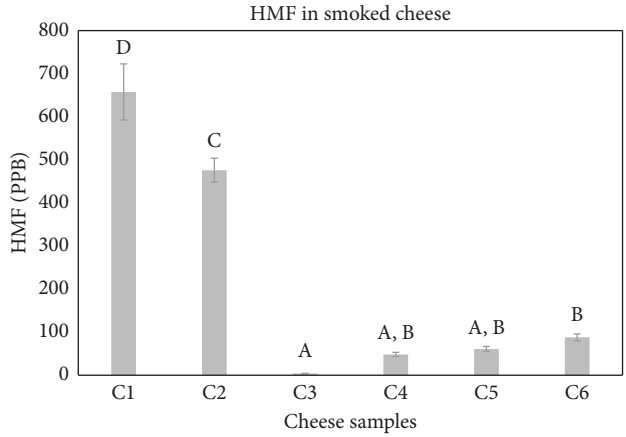

Figure 1: HMF concentration in smoked cheeses (Table 1 for sample details). Significant differences were determined by ANOVA analysis and Tukey test ($p \leq 0.05$). Different letters indicate significant differences ($n = 3$).

local area and most of it is hardwood. The lack of the brown rind may be indicative of the lower amount of HMF compared to samples C1 and C2. Between the two samples (C5 and C6), the triple smoked (C6) had a slightly higher concentration of HMF possibly due to the additional smoking. The difficulty of analysing cheese products could be related to the difficulty that Morales and Jiménez-Pérez [35] faced when analysing infant milk, which is the complexity of compounds in the heat-treated milk and the fact that other compounds were reported to coelute with HMF during chromatographic analysis. In addition, the heat treatment of milk before it is transformed to cheese may affect the HMF concentration as shown in the work of Magarinos et al. [36].

3.1.2. Occurrence of HMF in Processed Meat Products. For smoked processed meat, the different mean HMF concentrations and standard deviations are presented in Figure 2. Previous work has shown that HMF production is either a consequence of the presence of pentoses contributing to the Maillard reaction or from the dephosphorylation of ribose phosphate within the meat. Additionally, it has been observed that the level of acidity plays an important role in the extent of HMF production [37]. Sample M3 (German smoked peppered salami) had the highest mean HMF concentration (331 ppb). HMF concentrations found in samples M1 and M2 (oak smoked ham, 32 ppb, and beechwood smoked cooked ham, 46 ppb, respectively) were not significantly different ($p \leq 0.05$) from each other and were considerably lower when compared with the other meat samples. Samples M4 (German smoked ham, 169 ppb), M5 (Bavarian smoked ham, 171 ppb), and M6 (Italian smoked prosciutto, 180 ppb) showed no significant difference ($p \leq 0.05$) between their mean values.

3.1.3. Occurrence of HMF in Fish. For smoked fish samples, a slightly different sampling method was followed. As the skin of the selected fish was not edible, each sample was divided in flesh and skin and analysed as two individual samples (Figure 3). Fish products in general showed higher HMF concentration than the cheese and processed meat samples. Furthermore, in each sample, the flesh had significantly higher ($p < 0.05$) HMF concentration than the skin. For sample F1 (haddock), the flesh (F1-fl) had a mean concentration of 1202 ppb, while the skin (F1-sk) had a significantly lower mean concentration of 835 ppb. Sample F3 (salmon) showed corresponding results with a mean value for the flesh (F3-fl) of 1326 ppb and for the skin (F3-sk) 1011 ppb. ANOVA showed the amount of HMF in the flesh samples of F1-fl and F3-fl had no significant difference ($p > 0.05$). The results for sample F2 (mackerel) were significantly higher for the flesh (F2 fl) at 2930 ppb, while the skin F2-sk had a value that was not significantly different from F1-sk and F3-sk. For smoked fish products, hot smoking is the method that is most commonly used, unlike cheeses and processed meats which are generally cold smoked. There is a difference in the temperatures of these smoking processes (hot smoking is generally carried out at 55°C to 80°C and cold smoking at 15°C to 25°C [2, 4]), and this may be the explanation for the higher HMF concentration found in fish products. In addition, the burning matrix that was used for sample F3 was beechwood, a hardwood high in hexoses and pentoses, and the presence of which leads to the production of HMF during thermal treatment. It is also interesting to note that the smoked mackerel (F2) was a ready-to-eat hot-smoked product that has undergone thermal treatment equal to cooking. Pérez-Palacios et al. [38] recommended that fried fish should be included in high HMF concentration food groups and that generally the product handling and cooking procedure affects HMF levels. It is postulated that similar processes are at work here.

3.2. SPME-GC-MS Analysis and Results

3.2.1. Major Smoking Process-Related Compounds. Principal component analysis (PCA) was used to find a correlation between the concentration of HMF and some selected phenolic compounds. The presence and amounts of these phenolics are an indication of the degree of smoking the foods were exposed to and hence may be linked to HMF levels found. For this study, the phenolic compounds that

Table 1: Sample coding for all smoked products.

Smoked cheese					
C1 German smoked cheese	C2 Dutch smoked cheese	C3 Smoked metsovone	C4 Austrian smoked cheese	C5 Orkney single-smoked mature cheddar	C6 Orkney triple-smoked cheddar
Smoked processed meat					
M1 Oak smoked ham	M2 Beechwood smoked cooked ham	M3 German peppered smoked salami	M4 German smoked ham	M5 Smoked bavarian ham	M6 Italian smoked prosciutto
Smoked fish					
F1 Smoked haddock fillets	F2 Ready-to-eat smoked mackerel	F3 Hot-smoked salmon filets			

sk: skin; fl: flesh

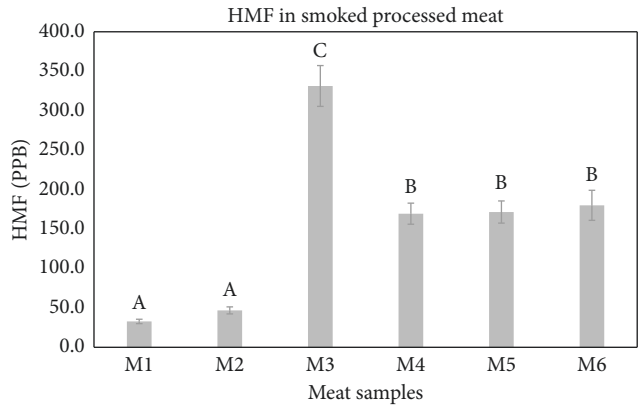

Figure 2: HMF concentration in smoked processed meats (Table 1 for sample details). Significant differences were determined by ANOVA analysis and Tukey test ($p \leq 0.05$). Different letters indicate significant differences ($n = 3$).

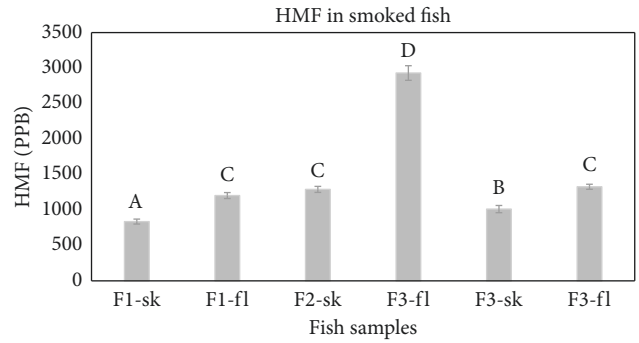

Figure 3: HMF concentration in smoked fish Table 1 for sample details). Significant differences were determined by ANOVA analysis and Tukey test ($p \leq 0.05$). Different letters indicate significant differences ($n = 3$).

were chosen to explore any potential relationships were syringol, eugenol, isoeugenol, guaiacol, *p*-cresol, and phenol because they are the major components identified in wood smoke, and previous studies have linked different wood types and smoking conditions with different concentration of these phenolic compounds [8]. For the cheese samples (Figure 4), a positive correlation was observed between HMF and syringol and *p*-cresol for C1 (smoked German cheese) and C2 (Dutch smoked cheese), and both of these are smoked using wood. When these are compared to C3 (metsovone smoked cheese) where the amount of phenolics was high, the product had the most intense smoky smell and flavour, but the HMF concentration was the lowest among the samples analysed. Taking into consideration the smoking procedure of this traditional smoked cheese (smoked with grasses, leaves, and herbs), it can be noted that while burning

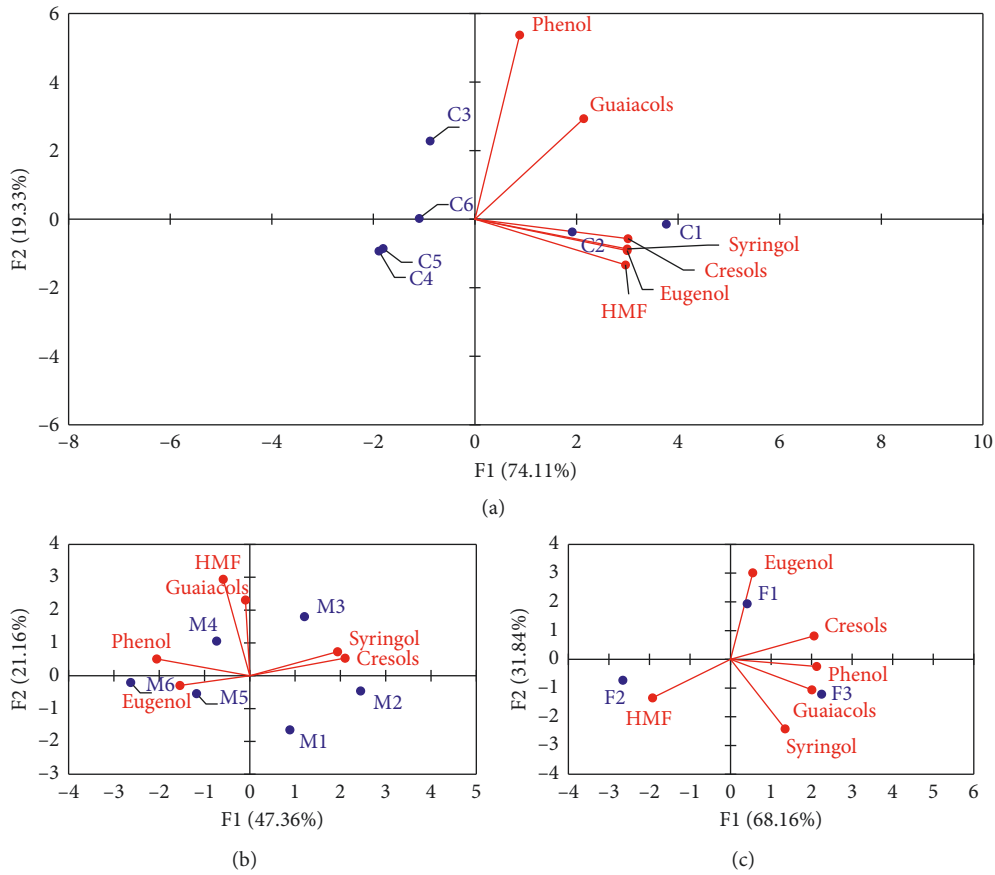

Figure 4: Principal component analysis of all smoked samples (PCA): (a) biplot of smoked cheese (axes F1 and F2: 93.44%); (b) biplot of smoked meat (axes F1 and F2: 68.52%); (c) biplot of smoked fish (axes F1 and F2: 100.00%).

herbs can also result to the production of phenolics, they do not consist of cellulose and hemicellulose which are found in wood and particularly associated with HMF formation [39]. A correlation between HMF and guaiacols and phenol was also in evidence for some meat samples. M3 (German peppered smoked salami) had the highest concentration of both HMF and these phenolics. Although fish samples in general had the highest HMF values, some of the phenolics (syringol, isoeugenol, and phenol) were found in very low concentrations, and so no correlation was found between HMF and phenolics in the fish samples analysed. Many factors seem to influence the amounts of phenolics in the smoked products. In previous studies of smoked fish, several major phenolic compounds were found for different smoking processes [40, 41]. Another factor that influences the smoky smell and flavour attributed to phenolic compounds are the type of wood, the burning temperature, the different smoke generation methods, and the fat content of the food. Lighter smokiness results from softer hardwoods that burn rapidly at low temperatures while for harder hardwoods, the opposite has been observed [42].

4. Conclusion

4.1. HMF. The measurement of HMF concentration in smoked cheese, smoked processed meat, and smoked fish was analysed with high-pressure liquid chromatography-coupled diode array detector (HPLC-DAD). The highest HMF concentration was shown in smoked fish samples, while cheese samples showed the widest range of results. After reviewing scientific data regarding different smoking processes such as the smoking temperature, smoking duration, and wood matrix, the variance of HMF concentrations was expected due to a variety of influencing factors [2, 4, 5, 7, 11, 13]. Traditionally, smoked fish is cooked by a hot smoking procedure, whereas cheese and processed meat are usually cold smoked at lower temperatures. There is a correlation between these smoking procedures and the level of HMF found with both cheese and processed meat having lower HMF levels. The fish sample with the highest HMF concentration was a ready-to-eat mackerel (F2) with a value of approximately 3000 ppb. Also, traditionally smoked metsovone cheese had the most intense smoky flavour and smell but with the lowest HMF concentration (4 ppb). The range of HMF concentration in smoked processed meat products was between 30 and 330 ppb (M1 and M3, respectively).

4.2. GC and Correlation. The PCA analysis of the potential correlation between HMF concentration and the amount of selected phenolic compounds discovered in smoked food products as a function of the smoking procedure was

conducted. The characteristic phenolic compounds discovered by SPME-GC-MS were syringol, guaiacol, eugenol, isoeugenol, *p*-cresol, and phenol. The investigation into a potential correlation between phenolics compounds and HMF was based on previous work that found that the abundance of phenolics (mainly from the pyrolysis of lignin in wood) in smoked produce is potential indicators of the duration and the temperature of the smoking process. A correlation was found between HMF concentration and the measured phenolics in cheese samples, while the correlation for fish and processed meat samples was not significant but indicative.

To conclude, the potential health effects due to HMF consumption have been investigated widely, and many studies have revealed the mutagenic and carcinogenic properties of the compound. The fact that there are no previous studies investigating HMF in smoked products make the findings of this research important as it can be used as a starting point for further investigation into the connection between HMF and smoking processes employed.

Data Availability

The data used to support the findings of this study are included within the article.

Disclosure

Part of this work was presented in the IMARS (ISMR13) meeting in Montreal (Canada) September 10–13, 2018.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

References

[1] S. Park, Y. Chung, Y. Lee, S. Yoon, J. Lee, and Y. Cha, "Quality properties of seasoned-dried pacific saury treated with liquid smoke-4. Quality stability of seasoned-dried pacific saury treated with liquid smoke during storage," *Fisheries and Aquatic Sciences*, vol. 5, no. 4, pp. 287–294, 2002.

[2] I. S. Arvanitoyannis and K. V. Kotsanopoulos, "Smoking of fish and seafood: history, methods and effects on physical, nutritional and microbiological properties," *Food and Bioprocess Technology*, vol. 5, no. 3, pp. 831–853, 2012.

[3] D. Baines, H. Griffiths, and J. Parker, "Smoking out carcinogens," *Food Science and Technology*, vol. 30, no. 2, pp. 36–39, 2016.

[4] P. J. Fellows, "17-smoking," in *Food Processing Technology*, P. J. Fellowspp. 525–537, Woodhead Publishing, Sawston, UK, 3rd edition, 2009.

[5] W. Sung, "Volatile constituents detected in smoke condensates from the combination of the smoking ingredients sucrose, black tea leaves, and bread flour," *Journal of Food and Drug Analysis*, vol. 21, no. 3, pp. 292–300, 2013.

[6] R. Tarté, *Ingredients in Meat Products*, Springer Science & Business Media, Vol. 10, Springer Science & Business Media, New York, NY, USA, 2009.

[7] J. A. Maga, "Contribution of phenolic compounds to smoke flavor," in *Anonymous*, ACS Publications, Washington, DC, USA, 1992.

[8] A. Hitzel, M. Pöhlmann, F. Schwägele, K. Speer, and W. Jira, "Polycyclic aromatic hydrocarbons (PAH) and phenolic substances in meat products smoked with different types of wood and smoking spices," *Food Chemistry*, vol. 139, no. 1–4, pp. 955–962, 2013.

[9] K. Abraham, R. Gürtler, K. Berg, G. Heinemeyer, A. Lampen, and K. E. Appel, "Toxicology and risk assessment of 5-hydroxymethylfurfural in food," *Molecular Nutrition and Food Research*, vol. 55, no. 5, pp. 667–678, 2011.

[10] J. Rufian-Henares and S. De la Cueva, "Assessment of hydroxymethylfurfural intake in the Spanish diet," *Food Additives & Contaminants: Part A*, vol. 25, no. 11, pp. 1306–1312, 2008.

[11] F. Shafizadeh and Y. Lai, "Thermal degradation of 1,6-anhydro-.beta.-D-glucopyranose," *Journal of Organic Chemistry*, vol. 37, no. 2, pp. 278–284, 1972.

[12] D. Shen and S. Gu, "The mechanism for thermal decomposition of cellulose and its main products," *Bioresource Technology*, vol. 100, no. 24, pp. 6496–6504, 2009.

[13] G. Ren, L. Zhao, Q. Sun, H. Xie, Q. Lei, and W. Fang, "Explore the reaction mechanism of the Maillard reaction: a density functional theory study," *Journal of Molecular Modeling*, vol. 21, no. 5, p. 132, 2015.

[14] H. Jaeger, A. Janositz, and D. Knorr, "The Maillard reaction and its control during food processing. The potential of emerging technologies," *Pathologie Biologie*, vol. 58, no. 3, pp. 207–213, 2010.

[15] A. Agila and S. Barringer, "Effect of roasting conditions on color and volatile profile including HMF level in sweet almonds (*Prunus dulcis*)," *Journal of Food Science*, vol. 77, no. 4, pp. C461–C468, 2012.

[16] V. Gökmen, Ö. Ç Açar, H. Köksel, and J. Acar, "Effects of dough formula and baking conditions on acrylamide and hydroxymethylfurfural formation in cookies," *Food Chemistry*, vol. 104, no. 3, pp. 1136–1142, 2007.

[17] N. Göncüoğlu and V. Gökmen, "Accumulation of 5-hydroxymethylfurfural in oil during frying of model dough," *Journal of the American Oil Chemists' Society*, vol. 90, no. 3, pp. 413–417, 2013.

[18] K. Kukurová, Z. Ciesarová, B. A. Mogol, Ö. Ç Açar, and V. Gökmen, "Raising agents strongly influence acrylamide and HMF formation in cookies and conditions for asparaginase activity in dough," *European Food Research and Technology*, vol. 237, no. 1, pp. 1–8, 2013.

[19] F. J. Morales and S. Jiménez-Pérez, "Hydroxymethylfurfural determination in infant milk-based formulas by micellar electrokinetic capillary chromatography," *Food Chemistry*, vol. 72, no. 4, pp. 525–531, 2001.

[20] A. Ramírez-Jiménez, B. García-Villanova, and E. Guerra-Hernández, "Hydroxymethylfurfural and methylfurfural content of selected bakery products," *Food Research International*, vol. 33, no. 10, pp. 833–838, 2000.

[21] H. Van Der Fels-Klerx, E. Capuano, H. Nguyen et al., "Acrylamide and 5-hydroxymethylfurfural formation during baking of biscuits: NaCl and temperature–time profile effects and kinetics," *Food Research International*, vol. 57, pp. 210–217, 2014.

[22] L. Zirbes, B. K. Nguyen, D. C. de Graaf et al., "Hydroxymethylfurfural: a possible emergent cause of honey bee mortality?," *Journal of Agricultural and Food Chemistry*, vol. 61, no. 49, pp. 11865–11870, 2013.

[23] T. Husøy, M. Haugen, M. Murkovic et al., "Dietary exposure to 5-hydroxymethylfurfural from Norwegian food and correlations with urine metabolites of short-term exposure,"

Food and Chemical Toxicology, vol. 46, no. 12, pp. 3697–3702, 2008.

[24] M. Bauer-Marinovic, F. Taugner, S. Florian, and H. Glatt, "Toxicity studies with 5-hydroxymethylfurfural and its metabolite 5-sulphooxymethylfurfural in wild-type mice and transgenic mice expressing human sulphotransferases 1A1 and 1A2," *Archives of Toxicology*, vol. 86, no. 5, pp. 701–711, 2012.

[25] B. H. Monien, H. Frank, A. Seidel, and H. Glatt, "Conversion of the common food constituent 5-hydroxymethylfurfural into a mutagenic and carcinogenic sulfuric acid ester in the mouse in vivo," *Chemical Research in Toxicology*, vol. 22, no. 6, pp. 1123–1128, 2009.

[26] C. Janzowski, V. Glaab, E. Samimi, J. Schlatter, and G. Eisenbrand, "5-Hydroxymethylfurfural: assessment of mutagenicity, DNA-damaging potential and reactivity towards cellular glutathione," *Food and Chemical Toxicology*, vol. 38, no. 9, pp. 801–809, 2000.

[27] C. Svendsen, T. Husøy, H. Glatt, M. Haugen, and J. Alexander, "5-sulfooxymethylfurfural (SMF), the metabolite of 5-hydroxymethylfurfural (HMF), increases the numbers of adenoma and aberrant crypt foci in the intestine of min-mice," *Toxicology Letters*, vol. 172, p. S202, 2007.

[28] D. Jöbstl, T. Husøy, J. Alexander, T. Bjellaas, E. Leitner, and M. Murkovic, "Analysis of 5-hydroxymethyl-2-furoic acid (HMFA) the main metabolite of alimentary 5-hydroxymethyl-2-furfural (HMF) with HPLC and GC in urine," *Food Chemistry*, vol. 123, no. 3, pp. 814–818, 2010.

[29] E. Capuano and V. Fogliano, "Acrylamide and 5-hydroxymethylfurfural (HMF): a review on metabolism, toxicity, occurrence in food and mitigation strategies," *LWT-Food Science and Technology*, vol. 44, no. 4, pp. 793–810, 2011.

[30] S. Pastoriza de la Cueva, J. Álvarez, Á. Végvári et al., "Relationship between HMF intake and SMF formation in vivo: an animal and human study," *Molecular Nutrition and Food Research*, vol. 61, no. 3, article 1600773, 2017.

[31] D. Özkök and S. Silici, "Effects of honey HMF on enzyme activities and serum biochemical parameters of Wistar rats," *Environmental Science and Pollution Research*, vol. 23, no. 20, pp. 20186–20193, 2016.

[32] A. Fiore, A. D. Troise, B. Ataç Mogol et al., "Controlling the Maillard reaction by reactant encapsulation: sodium chloride in cookies," *Journal of Agricultural and Food Chemistry*, vol. 60, no. 43, pp. 10808–10814, 2012.

[33] M. D. Guillén and M. C. Errecalde, "Volatile components of raw and smoked black bream (*Brama raii*) and rainbow trout (*Oncorhynchus mykiss*) studied by means of solid phase microextraction and gas chromatography/mass spectrometry," *Journal of the Science of Food and Agriculture*, vol. 82, no. 9, pp. 945–952, 2002.

[34] N. Montazeri, A. Oliveira, B. H. Himelbloom, M. B. Leigh, and C. A. Crapo, "Chemical characterization of commercial liquid smoke products," *Food Science and Nutrition*, vol. 1, no. 1, pp. 102–115, 2013.

[35] F. J. Morales and S. Jiménez-Pérez, "Effect of malondialdehyde on the determination of furosine in milk-based products," *Journal of Agricultural and Food Chemistry*, vol. 48, no. 3, pp. 680–684, 2000.

[36] H. Magarinos, M. Vargas, A. Romero, E. Carrasco, and S. Selaive, "Use of reconstituted concentrated nonfat milk for the production of UHT milk: physical and chemical effects and stability," *International Journal of Dairy Technology*, vol. 62, no. 2, pp. 182–188, 2009.

[37] M. S. Madruga and D. S. Mottram, "The effect of pH on the formation of maillard-derived aroma volatiles using a cooked meat system," *Journal of the Science of Food and Agriculture*, vol. 68, no. 3, pp. 305–310, 1995.

[38] T. Pérez-Palacios, C. Petisca, R. Henriques, and I. Ferreira, "Impact of cooking and handling conditions on furanic compounds in breaded fish products," *Food and Chemical Toxicology*, vol. 55, pp. 222–228, 2013.

[39] W. Baltes and I. Söchtig, "Nachweis eines Rauchar-omakondensatzusatzes zu Wurstwaren mit Hilfe der Glas-capillargaschromatographie," *Zeitschrift für Lebensmittel-Untersuchung und Forschung*, vol. 169, no. 1, pp. 17–21, 1979.

[40] T. Sérot and C. Lafficher, "Optimisation of solid-phase microextraction coupled to gas chromatography for determination of phenolic compounds in smoked herring," *Food Chemistry*, vol. 82, no. 4, pp. 513–519, 2003.

[41] T. Sérot, R. Baron, C. Knockaert, and J. L. Vallet, "Effect of smoking processes on the contents of 10 major phenolic compounds in smoked fillets of herring (*Cuplea harengus*)," *Food Chemistry*, vol. 85, no. 1, pp. 111–120, 2004.

[42] C. Saiz-Jimenez and J. De Leeuw, "Lignin pyrolysis products: their structures and their significance as biomarkers," *Organic Geochemistry*, vol. 10, no. 4–6, pp. 869–876, 1986.